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Dielectric relaxation of some polar molecules and their binary mixtures in non polar solvents

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Abstract : The dielectric absorption of 4-nitrobenzyl chloride, 1,2,3-trichloro benzene and cyclohexyl chloride, and their binary mixtures in CCl_4, decalin and a mixture of both solvents (1 : 1 by mole), have been studied over a wide range of frequency (0.2–18 GHz) and temperature (20–40°C) The data were analyzed according to Debye equation into one relaxation time. This relaxation could be attributed to the rotation of the molecule as a whole. The discrepancy in the value of these relaxation times either in the case of the individual monomers or in that of their binary mixtures when the viscosity of the solvent is taken into consideration, are interpreted according to the size of the solute when compared with that of the solvent.

Keywords : Dielectric relaxation, polar molecules, binary mixtures

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1. Introduction

Dielectric relaxation behaviour of polar molecules as well as their binary mixtures is of considerable importance for obtaining information about the relaxation processes. Only a few measurements on associating and non-associating polar molecules in non-polar solvents and even less information is available for simple systems [1]. Recently, Madan [1–4] studied the dielectric relaxation behaviour of some rigid polar molecules and their mixtures in dilute non-polar solvents.

In order to gain more information in this area, it is aimed to carry out a systematic study over a larger ranges of frequencies and temperatures. 4-Nitrobenzyl chloride, 1,2,3-trichloro benzene and cyclohexyl chloride, and their binary mixtures in dilute CCl_4, decalin and a mixture of both solvents (1 : 1 by mole) were chosen for that purpose. In addition, the temperature dependence of the dielectric relaxation time has been used to evaluate various molar activation energy parameters for dipole or orientation.

2. Experimental work

(i) Materials :

4-Nitrobenzyl chloride (Merck), 1,2,3-trichloro benzene (BDH), cyclohexyl chloride (Merck), carbontertrchloride (BDH) and decalin (Merck) were used as received.

(ii) Techniques :

The static permittivity ε_0 was measured at 2 MHz using a dipolemeter type DMO1 from wiss Tech. Wer werkstatten GMBH WTW, Germany. The instrument was calibrated using liquids of known permittivities.

The dielectric loss $\Delta\varepsilon''/x$ was measured in the frequency range 200 MHz up to 18 GHz using a sweep frequency spectrometer established at the National Research Centre, Cairo, Egypt, similar to that described by Hanna and Hammel [5]. The apparatus was calibrated every two weeks to be sure that it is working satisfactorily well with experimental error not exceeding 3%.

An abbe refractometer Carl Zeiss Jena, Germany model (G) was used to measure the refractive index n_D of the Na–D line to within 1×10^{-4} experimental error.

The viscosity η of the investigated solutions were measured using the unit AVS350 from 'Schott GERATE', Germany. In this case, the liquid meniscus is sensed optoelectrically at the measuring levels. These precision devices always ensure the high accuracy of the capillary viscometer. The viscosity measuring unit is connected with flow-through cooler CK100 to control the temperature to uncertainty of $\pm$ 0.1°C.

The temperature was controlled to within 0.5°C using an ultrathermostat.

3. Results and discussion

The dielectric loss $\Delta\varepsilon''/x$ for 4-nitrobenzyl chloride, 1,2,3-trichloro benzene and cyclohexyl chloride, have been measured over a frequency range of 0.6–18 GHz and temperatures between 20°C and 40°C. The measurements were carried out in dilute solutions of CCl_4 and decalin.

The data were analyzed according to Debye equation [6] into one Debye term. An example of the analyses is shown in Figure 1 for 4-nitrobenzyl chloride, in the different used solvents at different temperatures. The obtained relaxation times and their weight factors G are listed in Table 1. From this table, it is noticed that the weight factor G is less than unity for the three investigated molecules. It indicates that there is another absorption region in the higher frequency range. In case of 4-nitrobenzyl chloride, as the nitro group is considered to be unrotatable group [7], the second undetected relaxation mechanism could be due to the inner mobility of the molecule (*i.e.* the rotation of CH_3Cl [7].

On the other hand for cyclohexyl chloride, and 1,2,3-trichloro benzene, the value of G is found to be much higher than that of 4-nitrobenzyl chloride. In this case, the second

absorption region could be attributed to the polar absorption due to liberation of dipoles damped by soft collision [8].

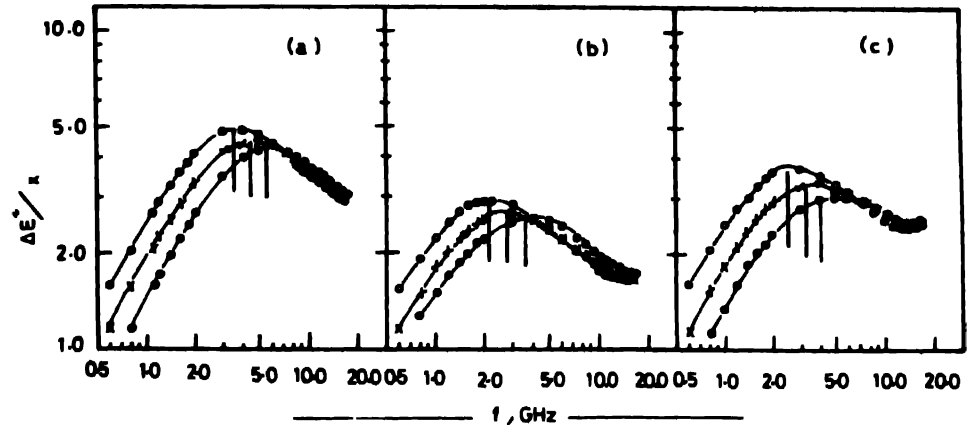

Figure 1. Absorption curves of 4-nitrobenzyl chloride at o 20°C × 30°C and ● 40°C in (a) CCl_4 (b) decalin and (c) decalin + CCl_4 (1 : 1 by mole).

The values of τ listed in Table 1 which are attributed to the rotation of the molecule as a whole, increase with increasing solvent viscosity. Relaxation times in solutions of

Table 1. Results of the analyses of the investigated molecules in CCl_4, decalin and CCl_4 + decalin mixture (1 : 1 by mole).

Material	solvent	t°C	τ pc	G	τ^*	ΔH k.cal/mol
4-Nitrobenzyl chloride	CCl_4	20	45.47	0.62	45.65	
		30	36 17	0.61	39.97	3.52
		40	28.94	0.61	36.49	
	Decalin	20	75.79	0,61	26.62	
		30	61.21	0.61	26.87	4.30
		40	44.21	0.60	23.13	
	CCl_4	20	63.66	0.61	37.42	
	+	30	49.74	0.60	34.10	3.75
	Decalin	40	40.81	0.59	32.64	
1,2,3-Trichloro benzene	CCl_4	20	15.92	0.95	15.98	
		30	13.26	0.93	14.65	3.10
		40	10.61	0.90	13.38	
	Decalin	20	24.49	0.88	8.60	
		30	19.89	0.87	8.73	3.75
		40	15.16	0.87	7.93	
	CCl_4	20	22.00	0.90	12.93	
	+	30	17.68	0.88	12.12	3.59
	Decalin	40	13.26	0.88	10.58	

Table 1. *(Cont'd.)*

Material	solvent	t°C	τ pc	G	τ^*	ΔH k.cal/mol
Cyclohexyl chloride	CCl_4	20	10.61	0.89	10.65	
		30	8.84	0.87	9.77	2.76
		40	7.33	0.86	9.24	
	Decalin	20	15.92	0.85	5.59	
		30	12.73	0.84	5.59	3.38
		40	10.27	0 84	5.37	
	CCl_4	20	14.47	0.89	8.51	
	+	30	11.79	0.88	8.08	3.07
	Decalin	40	9.95	0.87	7.94	

different viscosities should be compared only after a suitable viscosity correction has been applied [9]. A reduced relaxation time $\tau^* = \tau/\eta$ is thus defined to correct for viscosity differences and the values obtained are listed in Table 1. From this table, it is interesting to note that the values of τ^* in decalin are much lower than those in CCl_4. Since CCl_4 is considered to be an inert solvent, so this decrease of τ^* in decalin is not due to solute-solvent interaction but may be due to the small relative size of solute and solvent molecules [10]. The solute volume must appreciably exceed that of the solvent by a factor of about three times. This result is found to be comparable with the example provided by comparing 1,2-dichlorobenzene (a relatively small molecule) whose τ value increases by only 1.7 times in going from decalin to medicinal paraffin (η = 207CP) [10].

The molecules investigated were also measured on dilute solution of 1:1 by mole CCl_4 + decalin as a solvent mixture. The data obtained are listed in Table 1 together with the viscosity correction $\tau^* = \tau/\eta$. From this table, it is found that the value of τ^* of the investigated molecules in the solvent mixtures, lies between those for CCl_4 and decalin. It is interesting also to notice that the values of τ/η obtained in this case, is found to be higher than that in decalin but still lower than that in CCl_4. This is a reasonable result as the presence of decalin with its large size with respect to the solute is responsible for this result. On the other hand, this value is found to be little higher than the value evaluated from the presence of the solvent mixture in the ratio 1 : 1. This could be attributed to the difference in packing [11] of the solvent molecules around the investigated solutes.

The plot of $T\tau$ *versus* $1/T$ represents a good linear relationship within the experimental error from which the activation energy ΔH was calculated and listed in Table 1.

Three different systems concerning the binary mixtures (1 : 1 by mole) of :

(i) 4-nitrobenzyl chloride + 1,2,3-trichloro benzene,

(ii) 4-nitrobenzyl chloride + cyclohexyl chloride,

(iii) 1,2,3-trichloro benzene + cyclohexyl chloride,

are also studied in dilute solutions of CCl_4, decalin, and the mixtures of the two solvents (1 : 1 by mole). The measurements of $\Delta\varepsilon''/x$ were carried out at the same range of frequency and temperatures. The values of $\Delta\varepsilon''/x$ were analyzed and the data obtained are listed in Table 2. Examples of the analyses are shown in Figure 2 for 4-nitrobenzyl chloride and

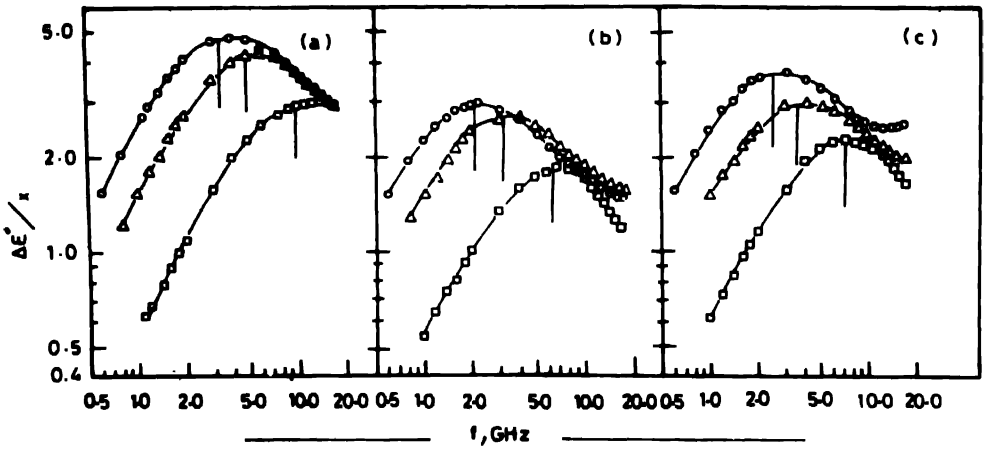

Figure 2. Frequency dependence of dielectric loss $\Delta\varepsilon''/x$ of o 4-nitrobenzyl chloride, O 1,2,3-trichloro benzene and Δ the mixture of the two components with 1 · 1 mole fraction at 20°C in (a) CCl_4 (b) decalin and (c) 1 : 1 by mole decalin + CCl_4.

1,2,3-trichloro benzene and the mixture of them at the different used solvents at 20°C. From this table, it is noticed that the first absorption region which is associated with the rotation of both molecules are represented by one relaxation mechanism. This is not surprising in

Table 2. Results of the analyses of the investigated mixtures in CCl_4, decalin CCl_4 + decalin mixture (1 : 1 by mole) at different temperatures.

Material	solvent	t°C	τ ps	G	τ^*	τ_{cal}	ΔH k.cal/mol
4-Nitrobenzyl	CCl_4	20	31.21	0.73	31.34	30.70	
chloride		30	25.26	0 73	27.92	24.72	3.44
+		40	20.67	0.71	26 07	19.78	
1,2,3-Trichloro	Decalin	20	51.34	0.77	18.03	50 14	
benzene		30	41.88	0.76	18.39	40.55	4.02
		40	30.61	0.76	16.02	29.68	
(1 : 1)							
	CCl_4	20	44.21	0.65	25.99	42.83	
	+	30	34.60	0.64	23.72	33 71	3.59
	Decalin	40	27.92	0.63	22.28	27.04	
4-Nitrobenzyl	CCl_4	20	28.94	0.72	29.06	28.04	
chloride		30	23.06	0.71	25.48	22.51	2.90
+		40	19.89	0.70	25.08	18.14	

Table 2. *(Cont'd.)*

Material	solvent	t°C	τ ps	G	τ^*	τ_{cal}	ΔH k.cal/mol
Cyclohexyl	Decalin	20	46.81	0.72	16.44	45.85	
chloride		30	37.89	0.71	16.64	36.97	4.10
		40	27.92	0.70	14.61	27.24	
(1 : 1)							
	CCl_4	20	40.81	0.65	23.99	39.07	
	+	30	31.83	0.64	21.21	30.77	3.60
	Decalin	40	25.67	0.63	20.48	25.38	
Cyclohexyl	CCl_4	20	14.47	0.93	14.53	13.27	
chloride		30	12.24	0.92	13.53	11.05	3.08
+		40	9.65	0.91	12 17	8.97	
1,2,3-Trichloro							
benzene	Decalin	20	21.00	0 89	7.38	20.20	
		30	17.68	0.88	7.76	16.31	3.56
(1 . 1)		40	13.26	0.88	6.94	12.71	
	CCl_4	20	18.72	0.89	11.01	17.91	
	+	30	15.91	0.88	10 91	14.42	3.25
	Decalin	40	12.24	0.87	9.77	11.53	

view of the fact that separate loss maxima are likely to appear only for different relaxation times $\tau 1$ and $\tau 2$ with a ratio $\tau 1/\tau 2 > 6$ [2]. From Table 2, it is interesting to notice that the relaxation time τ of all the mixtures are the average value of the relaxation times of the components, taking into consideration of the experimental error. This trend is similar to that found before in case of chlorobenzene-nitrobenzene systems [12]. This close agreement offers an evidence to the fact that each component retain their characteristic dielectric behaviour in the mixture; consequently, no complex formation is expected to take place in these mixtures. The reduced relaxation time $\tau^* = \tau/\eta$ for the investigated mixtures were estimated and listed in Tables 1 and 2. From the tables, it is found that τ^* is much higher in CCl_4 than in decalin which is the same trend found in the case of the investigated molecules.

The binary mixtures are also studied in dilute solution of 1 : 1 CCl_4 and decalin and the data are listed in Table 2. It is interesting to notice that the value of the relaxation time τ lies between those found for the individuals measured in the same solvent mixtures which indicate that there is no detected interaction between two components in the solvent mixture.

On the other hand, the activation energies ΔH for all the investigated mixtures were calculated and listed in Table 2. From this table, it is evident that ΔH for all the investigated

mixtures in the three different solvents lies between those for the individuals taking into consideration of the experimental error.

So from the dielectric relaxations and the activation energies, it could be concluded that the investigated molecules retain their characteristic dielectric behaviour in the mixture either in CCl_4, decalin or in the solvent mixture (1 : 1 CCl_4 + decalin).

References

[1] M P Madan *Can. J. Phys.* **26** 1573 (1987)

[2] M P Madan *Can. J. Phys.* **58** 20 (1980)

[3] M P Madan *J. Mol. Liq.* **25** 25 (1983)

[4] M P Madan *J. Mol. Liq.* **29** 161 (1984)

[5] F F Hanna and H Z Hammel *Phys. Chemie (Leipzig)* **263** 323 (1982)

[6] C P Smyth *Dielectric Behaviour Structure* (New York : McGraw Hill) (1955)

[7] S K S Somevanshi, S B L Misra and N K Mehrotra *Indian J Pure Appl. Phys* **16** 57 (1978)

[8] R Delker and G Klages Z *Naturforsch.* **A30** 611 (1981)

[9] R A Crump and A H Price *Trans. Farad. Soc.* **66** 92 (1970)

[10] N H Hill, W E Vaughan, A Price and M Davies *Dielectric Properties and Molecular Behaviour* (London : Von Nostrand) (1969)

[11] A M A Ghoneim *PhD Thesis* (Cairo University) (1982)

[12] F F Hanna, K N Abd-El-Nour and A M Ghoneim *Can. J Phys* **64** 1534 (1986)